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Remarks:

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divisional application to the application mentioned
under INID code 62.

(54) Glass-fiber compositions

(57) A biologically degradable glass-fiber composition characterized by the following constituents in percent by weight:

SiO ₂	45 to less than 57
Al ₂ O ₃	less than 2
CaO + MgO	10 to 16
Na ₂ O + K ₂ O	15 to 23
B ₂ O ₃	10 to 18
P ₂ O ₅	0 to 4
BaO	0 to 1
Diverse	0 to 2.

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Description

The present invention relates to a glass-fiber composition that is biologically degradable.

The prior art describes some glass-fiber compositions which are said to be biologically degradable.

The biological degradability of glass-fiber compositions is of great importance because various studies point out that some glass fibers with very small diameters in the range of less than 3 microns may be carcinogenic, while biologically degradable glass fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the glass fibers, or the products produced therefrom, the resistance of the glass fibers and the processibility of the glass-fiber composition. For example glass fibers are used to a great extent for insulation purposes. For these applications sufficient moisture-resistance is necessary.

Also, the glass-fiber composition must permit processibility by known methods for producing glass fibers with a small diameter, for example the centrifugal technique, in particular the inner centrifugal technique (this technique is described for example in US-PS 4 203 745).

The invention is based on the problem of providing a novel glass-fiber composition that is characterized by biological degradability, has good stability or resistance to moisture and is easy to process.

The invention is based on the finding that this problem can be solved by a glass-fiber composition that contains considerable amounts of alkali oxides and boron oxide, as well as optionally aluminum oxide.

It has turned out that such a glass-fiber composition fulfills the combination of the necessary properties, namely biological degradability, resistance to moisture and good processibility.

The object of the invention is a glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45 to less than 57
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	15 to 23
B_2O_3	10 to 18
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

The inventive glass-fiber compositions are processible by the centrifugal technique. The obtained fibers

have good resistance to moisture. Surprisingly enough, the glass-fiber compositions show biological degradability. The mean fiber diameter is preferably less than 10 microns and is in particular between 2.5 and 5 microns.

The inventive glass-fiber compositions preferably have the following constituents in percent by weight:

SiO_2	45 to less than 57
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	more than 18
B_2O_3	less than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

According to a further preferred embodiment the inventive glass-fiber compositions have the following constituents in percent by weight:

SiO_2	45 to less than 57
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	less than 18
B_2O_3	more than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

The inventive glass-fiber compositions preferably have less than 56.5 percent by weight silicon dioxide.

By adding aluminum oxide one can obtain an improvement in moisture-resistance. The inventive compositions are therefore preferably given at least 0.1 percent by weight, in particular at least 0.5 percent by weight, and usually less than 1.5 percent by weight aluminum oxide.

Biological degradability can be increased by the addition of phosphorus pentoxide. The inventive compositions therefore preferably contain at least 0.1 percent by weight P_2O_5 .

According to a further preferred embodiment the composition contains less than 2 percent by weight magnesium oxide.

The moisture-resistance of the inventive glass-fiber compositions was determined by a standard method known as the DGG method. In the DGG method 10 g

finely ground glass with a grain size between about 360 and 400 microns is held at the boiling point for five hours in 100 ml water. After quick cooling of the material the solution is filtered and a certain volume of the filtrate evaporated to dryness. The weight of the thus obtained dry material permits the amount of glass dissolved in the water to be calculated. The amount is stated in milligrams per gram of tested glass.

The biological degradability of the inventive glass compositions was tested by introducing 1 g of the glass powder, as described for the DGG method, into a physiological solution with the composition stated below and a pH value of 7.4:

NaCl	6.78
NH ₄ Cl	0.535
NaHCO ₃	2.268
NaH ₂ PO ₄ H ₂ O	0.166
(Na ₃ citrate) 2H ₂ O	0.059
Glycine	0.450
H ₂ SO ₄	0.049
CaCl ₂	0.022

Dynamic test conditions were selected as are described in Scholze and Conradt. The flow rate was 300 ml/day. The duration of the test was 14 days. The results are stated as percent of SiO₂ in the solution x 100 after 14 days.

The invention shall be described in more detail in the following with reference to examples.

Example 1

A glass of the following composition in percent by weight was melted:

SiO ₂	56.0
Al ₂ O ₃	1.0
CaO	9.0
MgO	4.0
Na ₂ O	18.0
K ₂ O	1.0
B ₂ O ₃	10.5
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 mg/g was determined.

The above-described test for biological degradability yielded a value of 550.

Example 2

A glass with the following composition in percent by weight was melted:

SiO ₂	55.0
Al ₂ O ₃	1.0
CaO	9.0
MgO	4.0
Na ₂ O	18.0
K ₂ O	1.0
B ₂ O ₃	10.5
P ₂ O ₅	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 3

A glass with the following composition in percent by weight was melted:

SiO ₂	56.5
Al ₂ O ₃	0.5
CaO	8.0
MgO	3.5
Na ₂ O	17.8
K ₂ O	0.2
B ₂ O ₃	12.0
P ₂ O ₅	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 50 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Claims

1. A glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO ₂	45 to less than 57
Al ₂ O ₃	less than 2
CaO + MgO	10 to 16
Na ₂ O + K ₂ O	15 to 23
B ₂ O ₃	10 to 18
P ₂ O ₅	0 to 4
BaO	0 to 1
Diverse	0 to 2.

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SiO ₂	45 to less than 57
Al ₂ O ₃	less than 2
CaO + MgO	10 to 16
Na ₂ O + K ₂ O	less than 18
B ₂ O ₃	more than 12
P ₂ O ₅	0 to 4
BaO	0 to 1
Diverse	0 to 2.

4. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO ₂	47 to less than 57
Al ₂ O ₃	less than 2
CaO + MgO	12 to 15
Na ₂ O + K ₂ O	16 to 20
B ₂ O ₃	10 to 16
P ₂ O ₅	0 to 2
BaO	0 to 1
Diverse	0 to 2.

5. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO ₂	52 to less than 57
Al ₂ O ₃	0 to 1.5
CaO + MgO	11 to 12.5
Na ₂ O + K ₂ O	16 to 18.5
B ₂ O ₃	10 to 14
P ₂ O ₅	0 to 1
BaO	0 to 1
Diverse	0 to 2.

6. The glass-fiber composition of any of claims 1 to 5, characterized in that the content of silicon dioxide is less than 56.5 percent by weight.
7. The glass-fiber composition of any of claims 1 to 6, characterized in that the content of aluminum oxide is at least 0.1 percent by weight.
8. The glass-fiber composition of any of claims 1 to 7, characterized in that the content of aluminum oxide is at least 0.5 percent by weight.
9. The glass-fiber composition of any of claims 1 to 8, characterized in that the content of phosphorus oxide is at least 0.1 percent by weight.
10. The glass-fiber composition of any of claims 1 to 9, characterized in that the content of boron oxide is more than 12 percent by weight.
11. The glass-fiber composition of any of claims 1 to 10, characterized in that the content of magnesium oxide is less than 2 percent by weight.

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P ₂ O ₅	0 to 4
BaO	0 to 1
Diverse	0 to 2.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 11 2380

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages		
A	EP-A-0 412 878 (SAINT GOBAIN ISOVER) 13 February 1991 * claims; examples * ---	1-11	C03C13/00
A	US-A-5 055 428 (PORTER RUSSELL M) 8 October 1991 * the whole document * ---	1-11	
A	GB-A-1 096 465 (UNITED STATES GYPSUM COMPANY) 29 November 1967 * claims; examples * ---	1-11	
A	EP-A-0 588 251 (SCHULLER INT INC) 23 March 1994 * claims 1-3; tables 1,2 * ---	1-11	
A	GLASTECHNISCHE BERICHTE, vol. 64, no. 1, 1 January 1991, pages 16-28, XP000178832 POTTER R M ET AL: "GLASS FIBER DISSOLUTION IN A PHYSIOLOGICAL SALINE SOLUTION" * page 26 - page 27; table 2 * ---	1-11	
L	EP-A-0 711 256 (SAINT GOBAIN ISOVER) 15 May 1996 ---		TECHNICAL FIELDS SEARCHED (Int.Cl.)
L	EP-A-0 711 257 (SAINT GOBAIN ISOVER) 15 May 1996 ---		C03C
L	EP-A-0 711 258 (SAINT GOBAIN ISOVER) 15 May 1996 -----		
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	12 November 1996	Van Bommel, L	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published no, or after the filing date		
A : technological background	D : document cited in the application		
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